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 C3P 10C13B 10C14B 10C17 10C20B 10C20C 10C20D1 10C9  
 10D2A 10K8 10T1X 11D2A1A 11K7 11T2X 14D2F  
 14D2H 14D3C1 14F2 14K7 14P1E1 14P2A1 14P4C  
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## (54) VESICULATED POLYMER GRANULES AND COATING COMPOSITIONS

(71) We, BALM PAINTS LIMITED of 1  
 Nicholson Street, Melbourne, Australia, a  
 Company organised and existing under the  
 laws of the State of Victoria, Common-  
 wealth of Australia, do hereby declare the  
 invention, for which we pray that a patent  
 may be granted to us, and the method by  
 which it is to be performed, to be particu-  
 larly described in and by the following  
 statement:

This invention relates to vesiculated poly-  
 mer granules and to coating compositions  
 comprising such granules.

It has been proposed to use particles of  
 certain polymers, for example poly(ethylene)  
 and poly(propylene) as insoluble compo-  
 nents of coating compositions and poly-  
 meric films. The particles, being of similar  
 refractive index to the medium in which  
 they are incorporated have little if any effect  
 on the opacity of films of the coating com-  
 positions or polymer films, when when of

[Price 25p]

suitable size they can disrupt the exposed 25  
 surfaces thereof to produce a matting of  
 texturing effect.

We have now found that polymer  
 granules prepared in a manner which im-  
 parts to them a vesiculated structure can be 30  
 utilised in coating composition and polymer  
 films to impart an opacity which is sur-  
 prisingly and usefully greater than that of  
 non-vesiculated granules of the same com-  
 position. Optionally the opacifying effect of 35  
 the granules may be further increased by  
 including particulate solids within the indi-  
 vidual vesicles. When the granules are  
 appropriately dimensioned they produce a  
 matting or texturing effect on the surface 40  
 of the films.

By vesiculated polymeric granules we  
 mean granules of polymer, preferably spher-  
 ical granules, which contain vesicles, the  
 walls of the vesicles being provided by the 45  
 polymer. Each granule comprises a plurality

of vesicles, that is it is not balloon-like, and although the vesicles are not necessarily of uniform size, the ratio of the diameter of the granule to the mean individual vesicle diameter should be at least 5 to 1. The vesicles should occupy from 5 to 95% of the total volume of the granules. Low vesicle volumes are usually associated with granules of high mechanical strength which are particularly useful for some applications, but to achieve the most useful opacifying effects we prefer that the vesicles occupy at least 20% of the total volume of the granules, preferably 20-75% of the volume.

Ideally each vesicle should be enclosed in a continuous shell of polymer, but it is not always easy nor is it essential to achieve this. For example, if the granules are produced directly in their required physical size and shape, e.g. by a suspension polymerisation process, there will be a random distribution of imperfect vesicles formed therein. On the other hand, if the granules are prepared by, for example, the mechanical degradation of bulk vesiculated polymer, substantially all of the vesicles adjacent to the outer surface of the granules will be imperfect; that is, part of the shell of polymer which preferably encloses them will be broken away.

Although the shape of the granules is not critical in achieving some increase in opacity in a film, we have found that a chunky or spheroidal structure gives the best results.

The mean diameter of the granules, as measured optically, is related to their end use but should be at least 1 micron. While granules having a mean diameter of 50 to 500 micron or more can be used to obtain texturing effects in films of coating compositions and polymer films, in general we find that granules having a mean diameter of 1 to 100 micron are of the most value as, for example, opacifying and opaque matting agents.

Preferably, when used as opaque matting agents, especially in coating compositions, the granules should have a mean diameter of 1 to 50 micron.

Bearing in mind the economic and practical limitations on the preparation and measurement of particulate solids, it is to be understood that the above limits comprehend the presence of a minor proportion, but not more than 10% by weight, of granules which lie outside the stipulated dimensions. Preferably, when used as opacifying or matting agents, essentially no granules should exceed the upper dimension limits by more than 20 micron.

The vesicles, which are roughly spherical in shape, should have a diameter of less than 20 micron and preferably less than 5 micron. The maximum acceptable diameter

will, of course, depend to a degree on the average diameter of the granule, but we have found that the opacifying effect of the granules tends to increase as the diameter of the individual vesicles decreases, the optimum light scattering effect of vesicles containing air being achieved in the range of 0.2-0.5 micron diameter.

The vesicles may be essentially gaseous; that is, they may be bubbles of air or other gas. In liquid coating compositions they may be saturated with vapour, for example with vapour diffusing into the vesicles through their polymeric walls from a liquid medium in which the granules are suspended, or may be at least partially filled with liquid for example, water or an organic liquid imbibed from the liquid medium in which the granules are suspended. When the granules are to be used in surface coatings, we prefer that any liquid in the vesicles be sufficiently volatile to diffuse out of the granules in contact with air. That is, when a coating film is formed on a substrate from the composition and dried in air, optionally at an elevated baking temperature, the granules provide essentially gaseous vesicles and in this physical form exert a preferred opacifying effect on the film.

In a further embodiment of the invention, the vesicles contain particulate solids. The particulate solids may be dispersed therein in a liquid in which the polymer is insoluble or may be associated in the vesicle with essentially gaseous components alone. For example, the vesicles may initially consist of particulate solids, e.g. particles of pigment, fungicide, insecticide or other toxic materials or blowing agents dispersed in a suitably volatile liquid which subsequently diffuses out of the granules to leave essentially dry pigment particles. We limit the particulate solids concentration for the performance of the invention to a maximum of 60% by volume of the vesicle but in practice we have generally found it economically desirable not to exceed our preferred concentration of 45% by volume of the volume of the vesicle.

Optionally, the polymer of the granule may itself be pigmented but in order to achieve a useful mechanical strength the degree of pigmentation must not exceed the critical pigment volume concentration. This parameter is a known physical transition point in pigment-binder systems and is defined, for example, in "Industrial and Engineering Chemistry," 41, 17, 1470 (1949).

Broadly speaking, the nature of the polymer is not critical provided it is insoluble in the coating composition in which the granules are to be used. Due regard must be paid in selecting the polymer to the conditions of temperature and mechanical stress to which it will be subjected in use.

For example, a granule comprising polymer which has a glass transition temperature substantially lower than that at which it is intended to be used may be irreversibly distorted and lose its characteristic vesiculated structure when so-used; which would be an unsatisfactory choice of polymer. To achieve adequate mechanical stability, especially when used in coating compositions where, for example, distortion of a coating film, e.g. by abrasion, may disfigure or rupture the film we prefer that the polymer, optionally pigmented, should be relatively rigid; that is, with an elongation at break of the order of 40% or less.

Suitable polymers are, for example, the condensation products of polycarboxylic acids with polyols; polycarboxylic acids with polyamines; caprolactam condensation products of the nylon 6 type; polyester amides; polyurethanes comprising the reaction products of polyisocyanates with polyols; polyethers; polyesters; epoxide and epoxy-amine resins; polyamides and ionic polymers such as nylon 66 salt.

Also suitable are condensates of formaldehyde with urea, melamine and phenols; esters of cellulose such as cellulose nitrate and cellulose acetate butyrate; chlorinated rubbers.

Our preferred polymers, however, are polymers and copolymers of  $\alpha,\beta$ -ethylenically unsaturated monomers and suitable monomers are, for example,

35 aromatic substituted ethylenes, e.g. styrene,  $\alpha$ -methyl styrene and vinyl toluene; optionally these may be copolymerised with a comonomer such as maleic anhydride or an unsaturated polyester;

40 vinyl acetate; saturated alcohol esters of acrylic and methacrylic acids, e.g. their methyl, ethyl and  $n$ -butyl esters; optionally these may be copolymerised with a comonomer such as acrylic or methacrylic acid; 45 esters and acid esters of unsaturated polybasic acids, e.g. the ethyl,  $n$ -butyl and 2-ethyl hexyl esters and acid esters of maleic and fumaric acids.

50 Preferably the toughness and hardness of the polymer is increased by introduction of a controlled degree of cross-linking. In the case of polymers prepared from  $\alpha,\beta$ -ethylenically unsaturated monomers, cross-

55 linking can be introduced by use of a di-functional comonomer. For example, a cross-linked copolymer can be formed by the addition polymerisation of methyl methacrylate monomer containing a minor proportion, e.g. 1 to 50% by weight of divinyl benzene or ethylene glycol dimethacrylate.

When the granules are required to release volatile liquid from the vesicles in contact 65 with air, due regard must be paid in the

selection of the polymer to its effect on the diffusion rate of the liquid. For example, while the polymer walls enclosing the vesicles are usually sufficiently thin to permit considerable latitude in selection of the polymer without markedly affecting the diffusion rate, a homopolymer of vinylidene chloride is relatively vapour impermeable. Some degree of control of diffusion of liquid can, therefore, be exercised by using 75 vinylidene chloride as a comonomer in preparing the polymer.

The particulate solids used in the granules may be pigment. The pigment is chosen from those commonly used in the art and 80 suitable pigments are, for example:

primary white pigments, that is opaque pigments with a refractive index of greater than 1.9, e.g. titanium dioxide, zinc oxide and antimony oxide; 85 extender pigments, e.g. calcium carbonate, silica, barium sulphate, alumina and naturally occurring aluminium silicates, e.g. kaolinite, dickite and montmorillonite, either singly or in combination.

90 The invention is not limited, however, to the use of the above types of pigment and unusual decorative effects may be produced in films by the use of granules in which only a part of the pigment used is coloured. 95 For example, the pigment may comprise iron oxide, phthalocyanine or lead chrome pigments.

The particulate solids need not, however, be pigment in the generally understood 100 meaning of the term. For example, the particulate solids may be anti-fouling or fungicidal materials, e.g. tri- $n$ -butyl tin fluoride, sodium pentachlorophenate and barium metaborate, insecticides, e.g. D.D.T. and 105 hexachlorbenzene, blowing agents or odorants. Alternatively the vesicles may contain liquids which have properties similar to these particulate solids. Such materials, when introduced directly into a film-forming polymer may have little opacifying effect on the 110 film and the choice of polymer is usually restricted by the requirement that the rate of leaching or diffusion of the material from the film must be limited. It is a particular 115 feature of our invention that when these materials are incorporated into the vesicles of the granules, especially as essentially dry particulate solids, they can contribute to the opacity of films in which the granules 120 are incorporated and also, by suitably selecting the polymer comprising the granules, a degree of control can be exercised over the leaching or diffusion rate of the particulate solids independent of the 125 characteristics of the film-forming polymer.

As stated above, the amount of particulate solids incorporated in the vesicles must not exceed 60% of the volume of the vesicles and while the size of the chosen 130

particles depends on the actual vesicle diameter, we prefer that the maximum particle diameter should be 1 micron.

The granules may be prepared by the mechanical degradation of suitable polymer in which vesicles have been implanted, for example, by the controlled aeration of bulk polymer. However, vesicles of the size we specify are not readily formed in a bulk polymer by, for example, direct aeration or foaming and our preferred method of preparing vesiculated polymer from polymerisable monomer is as follows. An incompatible liquid is dispersed throughout a polymerisable monomer, the diameter of the disperse particles being related to the size of the vesicles which are to be formed, and the monomer polymerised. The incompatible liquid is embedded in the polymer so-formed, in which it forms liquid vesicles. The polymer is mechanically ground to the required granule size and shape and when it is suitably volatile, the incompatible liquid may be removed, e.g. by vacuum extraction, to provide essentially gaseous vesicles. Similarly, when the incompatible liquid comprises particulate solids, vesicles which are essentially of particulate solids/liquid or particulate solids/gas may be formed. Preferably, a dispersion of an incompatible liquid in a polymerisable monomer may itself be dispersed in a liquid continuous phase in which the monomer is insoluble to form droplets of the required granule size and the monomer then polymerised to form vesiculated granules of the required dimensions. Optionally the granules can be separated from the liquid of the continuous phase and liquid removed from the vesicles as described above.

Alternatively instead of dispersing an incompatible liquid in the monomer, there may be dissolved in the monomer a liquid which is compatible with the monomer but incompatible with the polymer. When the dispersed droplets of monomer are polymerised the then incompatible liquid forms vesicles in the polymer particles.

As an alternative in both the above processes, a solution of polymer may be used in place of the monomer, the polymer granule then being formed not by polymerisation but by extraction of the solvent from the dispersed droplets of polymer solution.

The granules of the invention are particularly useful as components of surface coatings, in which they may be used, for example, to increase the polymer solids of the coating concurrent with an increase in opacity of films formed therefrom and as opaque matting and texturing agents.

We also provide therefore a coating composition comprising (a) a film-forming vehicle (b) a pigment dispersed in the vehicle

in a proportion of 0 to 85% of the total volume of (a) plus (b), and (c) insoluble vesiculated granules as hereinabove described said granules being dispersed in the composition in a proportion of 5 to 95% of the total solids (i.e. non-volatile) volume of the composition. Preferably the volume concentration of the granules is from 45 to 85% of the total solids volume. In the case of titanium dioxide the pigment volume is preferably 10 to 35% by volume of (a) plus (b).

By film-forming vehicle we mean film-forming polymer, optionally dissolved or dispersed in a suitable liquid and including other ancillary materials, e.g. catalyst, anti-skinning agents and dispersion stabilisers, commonly used in coating formulations. For example, the vehicle may be a solution or dispersion of film-forming polymer in an aqueous or organic liquid. Alternatively, the film-forming polymer itself may be present in the vehicle as precursor elements, usually at least in part polymeric, which when suitably catalysed or co-reacted form the film-forming polymer.

The choice of film-forming vehicle is not limited other than by the requirement that the vesiculated granules must be insoluble in it. For example, the vehicle may be an aqueous dispersion of poly(methyl methacrylate/ethyl acrylate) in which are to be dispersed vesiculated granules of polystyrene). A suitable vehicle for vesiculated poly(methyl methacrylate/ethylene glycol dimethacrylate) granules is, for example, a solution of a drying oil modified alkyd resin in an aliphatic hydrocarbon liquid.

Preferably, when the vehicle is a solution or dispersion of film-forming polymer in an aqueous liquid the vesicles contain an aqueous, optionally pigmented, liquid.

The granules are particularly useful in the preparation of matte aqueous latex paints of very low gloss. In this embodiment, we prefer that the granules be spheroidal, with a mean diameter essentially of from 1 to 50 micron and a volume average diameter of from 5 to 35 micron.

The volume average diameter is defined by the expression

$$\Sigma (V^i \cdot D^i)$$

where  $V^i$  is the volume fraction of all particles of diameter  $D^i$ .

By essentially of from 1 to 50 micron we mean that there may be present a minor proportion, not more than 10% by weight, of granules outside of these limits, preferably no granules (other than trace impurities) outside of these limits shall have a diameter of greater than 70 micron.

For the purpose of calculating the above coating composition limits, any granules of polymer having a diameter of less than 1 micron are included with the pigment

particles.

The vesiculated polymer granules of this invention may be incorporated in polymer to be formed into film by casting, extrusion or other processes. Where the film is to be cast from a solution of the polymer the granules must not be dissolved by the solvent of the solution. Where the film is to be formed by extrusion the polymer of the granules must have a Tg or softening point above the extrusion temperature. Granules of thermoset or cross-linked polymer are particularly useful in proportions of up to 25% by volume of the film. Preferably the granules are from 1 - 50 micron in diameter. The vesiculated granules may also be incorporated in bulk polymer in the form of castings, mouldings and extrusions in proportions of up to 60% by volume of the castings, mouldings, or extrusions. The vesiculated granules preferably of diameters less than 50 micron, may be used as filler in paper manufacture.

The invention is illustrated by the following examples in which all parts are given by weight:

#### Example 1

Preparation of vesiculated poly(styrene) granules with a volume average diameter of about 15 micron and containing approximately 50% by volume of one micron aqueous vesicles. A block of vesiculated poly(styrene) is first formed and then ground to the required granule size.

A surface active agent was prepared by reacting 19.7 parts of a solid copolymer of styrene/4-vinyl pyridine (42.9/2.5 by weight), 79.0 parts of propane sultone in a reaction vessel for three hours at 105°C.

To 22.0 parts of the above solution was added 22.0 parts of styrene and 1.1 parts of azodiisobutyronitrile. To this mixture was added slowly with continual high speed mechanical mixing 54.9 parts of a 2% by weight aqueous solution of a grade of hydroxyethyl cellulose which, as a 1% by weight solution in water had a viscosity of about 200 poise at 25°C.

A white, viscous emulsion of aqueous liquid in styrene was formed and this polymerised on heating at 95°C for five hours to a block of vesiculated poly(styrene) in which the vesicles were filled with the aqueous liquid. The polymeric block was broken up and ground in water in a laboratory pebble mill until the volume average diameter of the granules determined by microscopic examination was approximately 15 micron. The average vesicle diameter was similarly estimated to be about 1 micron and the calculated vesicle volume 50% of the granules. Although of somewhat irregular structure, the granules were of a chunky or spheroidal shape.

The suspension of granules in water from

the mill was concentrated by filtration to a solids content of 30.2% by weight (determined by heating for 60 minutes in an air oven at 150°C) to provide a slurry of granules identified as Granules Slurry No. 1.

#### Example 2

Preparation of vesiculated polymer granules similar to those of example 1 but in which the vesicles comprise aqueous liquid and rutile titanium dioxide.

A suspension of vesiculated granules in water was prepared by the general method of example 1 but replacing the 54.9 parts of 2% hydroxy ethyl cellulose of that example with a suspension of 38 parts of rutile titanium dioxide pigment in a mixture of 0.12 parts of sodium hexametaphosphate, 1.1 parts of hydroxyethyl cellulose (viscosity grade as example 1) and 62 parts of water.

The volume average diameter of the granules was estimated by microscopic examination to be about 15 micron and the shape similar to the granules of example 1. Electron micrographs confirmed the presence of *r*-titania within the vesicles, which had an average diameter of approximately 1 micron and maximum diameter less than 5 micron. The pigment volume concentration in the vesicles was estimated to be about 13% and the vesicle volume was approximately 52% of the total granule volume.

The suspension was concentrated to a solids content of 39.5% by filtration to provide a slurry of granules identified as Granules Slurry No. 2.

#### Example 3

In this example is described the preparation of vesiculated polystyrene granules by the emulsification of water droplets in styrene in the presence of a stabiliser, and the subsequent emulsion polymerisation of the styrene in an aqueous phase.

A latex of a 95/5 by weight styrene/dimethyl-amino-ethylmethacrylate copolymer quaternised with benzyl chloride (10.4 parts) in water (51 parts) stabilised with cetyl trimethyl ammonium bromide (0.53 parts) was mixed, using a high speed stirrer, with styrene (32 parts), divinyl benzene (3.6 parts), azodiisobutyronitrile (1.3 parts), sorbitan monostearate (3.0 parts), to produce a dispersion of water in monomer in which the disperse phase particles were about 2 micron in diameter and essentially free of particles greater than 3 micron diameter.

This dispersion was then emulsified in an aqueous phase consisting of partially hydrolysed poly(vinyl acetate) comprising approximately 20% of residual vinyl alcohol units and with a weight average molecular weight of about 1251000. (50 parts of a 10% by weight solution in water), hydroxy ethyl cellulose (50 parts of a 2.5% by weight

solution in water) and water (165 parts) using a conventional stirrer so as to avoid breakdown of the water in monomer dispersion. The emulsified particles of water-containing monomer were of diameter approximately 15 micron. The emulsion was heated in a closed pressure vessel at 90°C for three hours in a water bath to polymerise the particles of monomer. The resulting vesiculated polymer granules were added to water (4.5 parts), agitated and then allowed to settle to be recovered by decantation. Porosity measurements indicated that each granule had a vesicle volume of 21% of the total volume of the granule. It was confirmed that the average diameter of the granules and the average diameter of the vesicles were substantially the same as the average diameters of the emulsified water in monomer particles and disperse water particles respectively.

The granule diameter may be varied by varying the rate of stirring. At lower rates of stirring granules of diameter up to 500 micron were obtained with vesicle size 2 - 3 micron. The larger size granules contained a higher volume of vesicles, up to 60% by volume in the case of granules of diameter 500 micron. At higher rates of stirring the granule size was reduced to about 5 micron with a corresponding reduction in vesicle size. The volume of vesicles in the granules may also be varied by varying the proportion of water dispersed in the monomer.

#### Example 4

In this example there is described the preparation of vesiculated polystyrene granules in which pigment has been incorporated into the vesicles.

Rutile titanium dioxide (30 parts) was efficiently dispersed in water (20 parts) in the presence of sodium hexametaphosphate (0.4 part). Sufficient water was then added to this dispersion to provide the relative volume of pigment, based on the total volume of pigment and water, required in the final vesicle. In this case the pigment content of the vesicle was to be 10% by volume and the above dispersion (25.2 parts) was mixed with water (10 parts) to provide this pigment content, together with 0.880 ammonia (1 part).

23 parts of 95/5 by weight styrene/hydroxyethyl methacrylate copolymer in which each hydroxyl group has been reacted with maleic anhydride to produce a half ester, were dissolved in a mixture of azodiisobutyronitrile (1.3 parts), styrene (32 parts), and divinyl benzene (3.6 parts), and into the product was emulsified the above aqueous pigment dispersion using a high speed stirrer. The resulting emulsion was then emulsified in an aqueous phase consisting of partially hydrolysed poly (vinyl acetate)

according to Example 3 (50 parts of 10% by weight solution in water), hydroxyethyl cellulose (50 parts of a 2½% by weight solution in water) and water (165 parts) using a conventional stirrer. The final emulsion was polymerised in a closed pressure vessel heated at 90°C for three hours in a water bath. The resulting pigmented granules were washed and decanted. The average granule diameter was estimated to be 12 micron and the average vesicle diameter to be 2 micron. The vesicle volume was found to be 34% based on the total volume of granule which had a maximum diameter of about 18 micron.

It was confirmed by the use of the scanning electron microscope that pigment was present in the vesicles.

Repeating this process but varying the pigment content of the vesicle, suitable adjustment of the proportion of titanium dioxide in the initial pigment dispersion and varying the average granule and vesicle diameters by adjustment of the rates of stirring employed, granules with the following characteristics were prepared:

Average granule diameter micron	Average vesicle diameter micron	Vesicle volume %	Pigment content as % of vesicle volume
14	3	27	0.5
15	3	23	1.1
18	3-4	25	7.5
15	3	22	5.0
12	2	20	10.0
20	4-5	16	26.5
22	4	12	40.0
20	4	25	11.0

The results in the above table show that by adjusting the manufacturing procedure, pigment loadings of up to 40% by volume could be introduced into the vesicles of these granules, all of which vesicles had maximum diameters of less than 20 micron. The particle/mean vesicle ratios of samples 1, 3 and 6 of the table were measured photomicrographically to be approximately 5/1 although the ratios calculated from the estimated average granule and vesicle diameters were marginally lower.

#### Example 5

In this example there is described the preparation of vesiculated polystyrene granules in which the polymer has been pigmented.

Rutile titanium dioxide (13.6 parts) was efficiently dispersed in a mixture of divinyl benzene (3.6 parts) and styrene (32 parts) in which had been dissolved 23 parts of the copolymer half-ester described in example 4. Azodiisobutyronitrile (1.3 parts) was then added to the dispersion and the dispersion emulsified with water (22 parts) and 0.880 ammonia (1 part) using a high speed stirrer.

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The resulting emulsion was then emulsified in an aqueous phase containing a partially hydrolysed poly (vinyl acetate) according to Example 3 (50 parts of a 10% by weight solution in water), hydroxyethyl cellulose (50 parts of a 2½% by weight solution in water) and water (165 parts) with a conventional stirrer. This emulsion was polymerised at 90°C for three hours in a closed pressure vessel.

The resulting vesiculated polystyrene granules were washed in water by decantation.

The granules contained 5% of pigment by volume based on the volume of polymer in the granule and the use of the scanning electron microscope confirmed that the pigment was present in the polymer rather than in the vesicles.

It was estimated that the average granule diameter was 22 micron and that the average vesicle diameter was 4 micron. The vesicle volume of the granules was 16% based on the total granule volume and the maximum vesicle diameter less than 12 micron.

The process was repeated using different amounts of titanium dioxide and stirring speeds to give granules with the following characteristics:

*Sample 1:* Average granule diameter 15 micron, average vesicle diameter approximately 3 micron, vesicle volume 20%, maximum vesicle size 8 micron, polymer 0.27% pigment by volume.

*Sample 2:* Average granule diameter 30 micron, average vesicle diameter 3 micron, vesicle volume 18%, max. vesicle size about 10 micron, polymer 15% pigment by volume.

#### Example 6

In this example there is described the preparation of vesiculated poly(styrene) granules with a volume average diameter of about 15 micron and in which both the vesicles and the polymer contain rutile titanium dioxide.

A surface active agent was prepared by reacting a styrene/methacrylic acid copolymer (25.8/0.74 by weight) with 0.4 parts of a condensate of epichlorhydrin and diphenylolpropane which had an epoxide equivalent of about 190 and a viscosity of 125 poise at 25°C. The agent was prepared as a 32.9% by weight solution in styrene which had a viscosity of 6.6 poise at 25°C.

Using a high-speed mixer, 25.0 parts of rutile titanium dioxide were dispersed into a mixture of 17.5 parts of the above solution and 12.5 parts of styrene to give dispersion (a).

A suspension of 22.5 parts of rutile titanium dioxide in a mixture of 18.9 parts of water and 3.6 parts of triethanolamine was emulsified into dispersion (a) using a high-

speed mixer, to form a viscous, white emulsion, dispersion (b).

Dispersion (b) was added in bulk to a solution of 0.45 parts of hydroxyethyl cellulose (viscosity grade as in example 1) and 0.6 parts of an 88% hydrolysed grade of poly(vinyl acetate) of weight average molecular weight approximately 125,000 in 69.95 parts of water. The mixture was mechanically stirred at a rate which formed in 3 minutes emulsified particles of dispersion (b) having a volume average particle diameter of about 15 micron; dispersion (c).

To dispersion (c) was added 0.75 parts of azodiisobutyronitrile and the styrene polymerised by heating the charge to 70°C in a reaction vessel fitted with a stirrer and reflux condenser, for ten hours. The charge was then diluted with 2000 parts of water and allowed to settle for two days. The sedimented granules were concentrated to an aqueous slurry of 34.2% by weight solids content as determined by the method of example 1.

Microscopic examination of the granules confirmed the presence of rutile titanium dioxide in both the polymer and the vesicles, the volume average diameter of the granules being approximately 15 micron.

It was estimated that the granules contained approximately 30% by volume of vesicles and that the vesicles contained about 15% by volume of rutile titanium dioxide. The average vesicle size was estimated by microscopic examination of dispersion (b) to be about 1 micron and the maximum vesicle size about 3 micron.

#### Example 7

In this example there is described the preparation of vesiculated unsaturated polyester/styrene granules by a method similar to that used in example 3.

To 30 parts of a 58% by weight solution in styrene of an unsaturated polyester based on fumaric acid, phthalic anhydride and propylene glycol (approximately 3:1:4 by moles) was added 1.8 parts of an 86/14 by weight copolymer of vinyl acetate and dimethylaminoethyl methacrylate quaternised with benzyl chloride, and 0.6 parts of benzoyl peroxide. Water (15 parts) was added to this solution using a high-speed stirrer to produce a dispersion of water droplets in the polymer solution, in which the disperse phase water droplets had a maximum diameter of 4 micron.

The dispersion was then emulsified into an aqueous phase consisting of a partially hydrolysed poly (vinyl acetate) according to Example 3 (20 parts of a 13.6% by weight solution in water), hydroxyethyl cellulose (100 parts of a 2.25% by weight solution in water) and water (230 parts) to give emulsified particles of water-containing polyester/styrene droplets of average diameter 25 mic-

ron. The emulsion was heated in a closed pressure vessel at 90°C for 5 hours. The resulting vesiculated polymer granules were washed with water and recovered by settling.

The vesicles in the granules occupied approximately 40% of the total volume of the granules, and had an average diameter of approximately 3 micron. The average granule diameter was 25 micron.

On repeating the process and incorporating pigment in the vesicle by the process of example 4, granules were obtained having the following characteristics: granule diameter 40 micron, average vesicle diameter 5 micron, vesicle volume 15.9%, pigment content 10% of vesicle volume. In both samples the maximum vesicle diameter was less than 12 micron.

#### Example 8

This example describes the preparation of vesiculated epoxy-amide granules using a method similar to that described in example 3 but in which water has been replaced by aliphatic hydrocarbon.

100 parts of the liquid epichlorhydrin condensate used in example 6 were well mixed with 100 parts of a liquid polyamide having free amine groups (amine value 400 equivalent mgms KOH/gm.). In the resulting liquid was finely dispersed a solution of 1:1 by weight graft copolymer of methyl methacrylate backbone of molecular weight 5000 and side chains of polyhydroxystearic acid molecular weight (12.3 parts of a 32.5% by weight solution in aliphatic hydrocarbon) and then aliphatic hydrocarbon (b.p. 130°C) (62 parts).

This dispersion was then itself dispersed in a mixture of aliphatic hydrocarbon (300 parts) and graft copolymer as used above (9.24 parts) to produce aliphatic hydrocarbon-containing droplets of epoxy-amide resin of average diameter 10-20 micron. The emulsion was agitated for 2-3 hours to maintain discrete droplets during polymerisation at room temperature.

The resulting vesiculated granules were separated and it was estimated that the average vesicle diameter was 1 micron and the average granule diameter was 10-20 micron. The granules comprised about 25% by volume of vesicles of maximum diameter less than 3 micron.

#### Example 9

This example describes the preparation of vesiculated cellulose acetate butyrate granules.

5 parts of white spirit were added to a solution of 10 parts of cellulose acetate butyrate in 90 parts of ethyl acetate. The solution was then dispersed in an aqueous phase consisting of water (16.5 parts), a partially hydrolysed poly (vinyl acetate) according to Example 3 (50 parts of a 10%

solution in water), hydroxy ethyl cellulose (50 parts of a 2½% solution in water), and ethyl acetate (26.5 parts).

The dispersion of the cellulose acetate butyrate solution was diluted with a large quantity of water to leach out ethyl acetate whereupon the white spirit precipitated out in the cellulose acetate butyrate to form small vesicles.

The vesiculated granules were isolated and estimated to have an average vesicle diameter of 1 micron and an average granule diameter of 5 - 10 micron. The granules contained about 40% by volume of vesicles which had substantially uniform diameter of about 1 micron.

#### Example 10

In this example is described the preparation of vesiculated methyl methacrylate copolymer granules by the dispersion of water droplets in a methyl methacrylate copolymer solution and the subsequent emulsification of this dispersion into a water phase, and extraction of the solvent.

16.2 parts of an 86/14 by weight copolymer of methyl methacrylate and dimethyl amino ethyl methacrylate quaternised with benzyl chloride, were dissolved in toluene (40.0 parts). The solution was added to water (50.0 parts) using a high dispersion speed stirrer to produce a dispersion of water droplets in the polymer solution in which the disperse phase water particles had a maximum diameter of 4 micron.

This dispersion was emulsified in an aqueous phase consisting of a partially hydrolysed poly (vinyl acetate) according to Example 3 (11 parts of a 13.6% by weight solution in water), hydroxy ethyl cellulose (55 parts of a 2.25% by weight in water) and water (133 parts) using a conventional stirrer. The emulsified particles of water-containing polymer solution were of average diameter approximately 35 micron. The toluene was extracted from the particles by stirring the emulsion with an aliphatic hydrocarbon (500 parts), and the resulting vesiculated polymer granules diluted with water (4000 parts) recovered by decantation and dried. Porosity measurements indicated that the granules had a vesicle volume of 61% of the total volume of the granules. The maximum diameter of the vesicles was 4 micron and the average granule diameter was approximately 25 micron.

#### Example 11

The process of example 10 was repeated but instead of the methyl methacrylate copolymer, a commercial grade of chlorinated rubber was used. The vesicles occupied 39% of the total granule volume, and had a maximum diameter of 10 micron. The average granule diameter was 20 micron and

the average vesicle diameter about 4 micron.

#### Example 12

In this example granules were prepared by the process of example 10 but instead of the methyl methacrylate copolymer, a commercial grade of vinylidene chloride-acrylonitrile copolymer was used, and instead of toluene, a mixture of amyl acetate and methylethyl ketone (120 parts of a 1:1 by weight mixture) was used. Triethanolamine (0.5 parts) was added to the water dispersed into the polymer solution. Instead of being extracted the solvents were distilled off. The vesicles in the granules occupied approximately 30% of the total granule volume, and had a maximum diameter of slightly less than 20 micron. The average granule diameter was 60 micron and the average vesicle diameter about 11 micron.

#### Example 13

In this example is described the preparation of vesiculated styrene copolymer granules by a process similar to that given in example 10, but extracting the solvent by dilution with an excess of water. By dispersing a large quantity of water into the polymer solution highly porous granules were obtained.

40 parts of a 92/8 by weight copolymer of styrene and dimethyl amino ethyl methacrylate quaternised with benzyl chloride were dissolved in butyl acetate (100 parts) and water (300 parts) were slowly added using a high-speed mixer to produce a dis-

Parts Styrene Copolym.	Parts Butyl Acetate	Parts Water Dispersed	Average Granule Diam.	Maximum Vesicle Diam.	Vesicle Vol. of Granules
6.7	40.0	133	150 micron	10 micron	89%
5.0	42.0	150	75 micron	20 micron	95%

The vesiculated granules having a vesicle volume of 95% were extremely fragile. The average vesicle diameters were 7 and 13 micron respectively.

#### Example 14

In this example is described the preparation of vesiculated poly cyclohexylmethacrylate granules by a process incorporating elements of examples 3 and 12.

11.5 parts of a 92/8 by weight copolymer of cyclohexylmethacrylate and dimethyl amino ethyl methacrylate quaternised with benzyl chloride and azodiisobutyronitrile (11 parts) were dissolved in a mixture of cyclohexyl methacrylate (36 parts) and toluene (40 parts), and water (70 parts) was slowly added using a high-speed mixer to produce a dispersion of water droplets in the polymer solution.

The dispersion was then emulsified into an aqueous phase consisting of partially

persion of water droplets in the polymer solution.

This dispersion was emulsified in an aqueous phase consisting of partially hydrolysed poly (vinyl acetate) according to Example 3 (28 parts of a 13.6% by weight solution in water), hydroxy ethyl cellulose (140 parts of a 2.25% by weight solution in water), water (332 parts) and butyl acetate (6 parts) to give emulsified particles of water-containing polymer solution of average diameter 200 micron. Butyl acetate was extracted from the particles by diluting the emulsion with water (3000 parts), and the resulting vesiculated granules were allowed to settle, recovered by decantation and dried. Porosity measurements indicated that the granules had a vesicle volume of 76% of the total volume of the granules. The maximum diameter of the vesicle was 5 micron, and the average granule diameter was approximately 150 micron.

The process was repeated but the amounts of styrene copolymer and butyl acetate in the initial solution, and the amounts of water dispersed into the solution were those listed below. Furthermore, the water-containing polymer solution was emulsified into an aqueous phase consisting of hydroxyethyl cellulose (25 parts of a 2.25% by weight solution in water), water (275 parts) and butyl acetate (3 parts). The average granule diameter, the maximum vesicle diameter and the vesicle volume concentration of the granules obtained were as follows:

hydrolysed poly (vinyl acetate) according to Example 3 (20 parts of a 13.6% by weight solution in water), hydroxyethyl cellulose (100 parts of a 2.25% by weight solution in water) and water (230 parts) to give emulsified particles of water-containing polymer solution of average diameter 20 micron. The emulsion was heated in a glass vessel fitted with stirrer and condenser, and the toluene was slowly removed by distillation over a period of 4 hours. Polymerisation of the monomer occurred simultaneously.

The resulting polymer granules were diluted with water allowed to settle and recovered by decantation. Porosity measurements indicated that the granules had a vesicle volume of 15% of the total volume of the granules. The maximum diameter of the vesicles was 4 micron with a mean diameter of under 2 micron. The average granule diameter was approximately 10 micron.

*Example 15*

This example describes the preparation of vesiculated methyl methacrylate copolymer granules by the dispersion of aqueous droplets in a methyl methacrylate copolymer solution and the subsequent emulsification of this dispersion into a water phase and extraction of the solvent. The vesicles contain the fungicide sodium pentachlorophenate.

A slurry of vesiculated granules was prepared by the general method of example 10 but replacing all of the water of that example with an equal weight of a 2% by weight solution in water of sodium pentachlorophenate. The slurry was allowed to settle, the supernatant liquid was decanted and the granules washed and dried. The maximum diameter of the vesicles was about 5 micron and the average granule diameter approximately 25 micron. The vesicle volume of the granules was estimated to be about 60% of the total granule volume.

A slurry of the granules in distilled water was allowed to stand for 24 hours and the presence of sodium pentachlorophenate leached into the water confirmed analytically. The granules were transferred into a fresh quantity of distilled water and the process repeated. After several days, sodium pentachlorophenate continued to leach from the granules into the freshly added water. That is, despite the high solubility of sodium pentachlorophenate in water, its availability was modified by placing the phenate within the vesicles of the granules.

*Example 16*

Preparation of an aqueous latex coating composition comprising vesiculated granules from example 1. The pigment volume of the composition is 30% and the volume of vesiculated granules 86%; as defined above.

A mill-base was prepared by blending together for 30 minutes in a high-speed mixer the following components:

	rutile titanium dioxide	8.4 parts
	25% (w/w) aqueous solution of a commercial anionic polymeric surface active agent	0.4 part
50	1,2-propylene glycol	2.9 parts
	commercial anti-foaming agent (sodium salt of condensed aryl sulphonic acid)	0.1 part
55	To the mill-base so-prepared were added with stirring and in the order given, the following:	
	aqueous acrylic copolymer latex, 46.5% solids (wt.) and particle diameter approximately 0.4 micron	12.20 parts
60	quaternary ammonium type anti-microbial agent	0.04 part
65	water	1.30 parts

	ethylene glycol mono- <i>n</i> -butyl ether	0.60 part
	di-octadecyl sodium sulphosuccinate	0.04 part
	Granules of example 1	74.00 parts

The paint so-prepared was brushed out onto a coloured non-porous substrate and dried to a white, opaque film. The opacity was greater than that associated with a similar film of the same overall composition and pigment content but containing no vesiculated granules.

*Example 17*

Preparation of an aqueous latex coating composition comprising vesiculated granules from example 2. The pigment volume of the composition is 33% and the volume of vesiculated granules 88%; as defined above.

A mill-base was prepared by blending together for 30 minutes in a high-speed mixer the following components:

	rutile titanium dioxide	7.0 parts
	25% (w/w) aqueous solution of sodium hexametaphosphate	0.1 part
	water	2.1 parts

To the mill-base so-prepared were added with stirring and in the order given, the following:

	anionically stabilised acrylic copolymer latex, solids 46.5% and particle size approximately 0.1 micron	8.5 parts
	water	7.1 parts
	granules of example 2	75.2 parts

The paint so prepared was brushed out onto a coloured, non-porous substrate and dried to a white, opaque film. The opacity was greater than that associated with a similar film of the same overall composition and pigment content but containing no vesiculated granules.

*Example 18*

Preparation of an aqueous latex coating composition comprising vesiculated granules from example 6. The pigment volume of the composition is 29% and the volume of vesiculated granules 77%; as defined above.

To 79.8 parts of granules made in example 6 was added 7.0 parts of rutile titanium dioxide and the mixture subjected to high speed stirring for 10 minutes. The stirring speed was then reduced and 10.4 parts of an ionically stabilised acrylic copolymer aqueous latex (solids 46.5%, approximately particle diameter 0.1 micron) together with 2.7 parts of a 2.5% (w/w) aqueous solution of hydroxyethyl cellulose (viscosity grade as example 1) added.

The paint so-prepared was brushed out onto a coloured, non-porous substrate and dried to a white matt film of high opacity.

*Example 19*

A coating composition was prepared by

first dispersing rutile titanium dioxide (62 parts) in water (160 parts) in the presence of sodium hexametaphosphate (0.6 part) and then mixing the dispersion with a commercially available acrylic latex (258 parts of a 46% solids latex; AC - 34 ex Rohm & Haas).

A portion of the paint was well mixed with vesiculated pigmented granules made according to example 4, the volume proportion of granules being equal to the total solids of the paint. This granule-containing paint was applied as a film to a glass surface and compared for opacity with a similar film of the paint which did not contain granules. The scatter coefficient was determined using the Kubelka Munk method and the ratio of this to pigment volume concentration calculated in the absence of polymer granules was 137 for the standard

paint.

#### Example 20

Preparation of four matt aqueous latex paints comprising different vesiculated polymer granules.

Titanium dioxide (12.1 parts) and sodium hexametaphosphate (0.06 parts) were added to an aqueous slurry of vesiculated granules (66.4 parts, granule content 18% by weight) and the mixture stirred with a high-speed mechanical disc agitator for 30 minutes. Silica (0.84 part) and 1,2-propylene glycol (3.40 parts) were added and stirring continued for 10 minutes, when the stirring speed was lowered to reduce aeration and the aqueous latex of acrylic copolymer (17.2 parts, 46.5% copolymer) added.

The paints differed in using granules of the following characteristics, granule (a) being a preferred type:

	Vesiculated Granules	Paint Sample			
		(a)	(b)	(c)	(d)
		micron	micron	micron	micron
45	Approximate diameter	1-48	1-128	1-45	1-45
	Vol. average dia.	25	20	approx. 3	25
50	Vesicle dia.	approx. 1	approx. 1	approx. 0.5	approx. 1.5
	Vesicle volume	50%	50%	50%	50%
	Elong. at break of polymer	under 10%	under 10%	under 10%	over 80%
	Composition of polymer in granules				
55	titanium dioxide	10% by wt.	10% by wt.	10% by wt.	10% by wt.
	polymer	poly(methyl methacrylate)	poly(methyl methacrylate)	poly(methyl methacrylate)	poly (2-ethyl hexyl acrylate/divinyl benzene)
60					(95/5 by wt.)

All granules had maximum vesicle diameter of less than 5 micron.

Films of each paint were applied by brush to glass panels at a spreading rate of approximately 600 sq. ft. per gallon and allowed to dry in air at 25°C and 50%

relative humidity. All compositions formed coherent, dry films in less than one hour. Some properties of the dry films were as follows:

	Sample	(a)	(b)	(c)	(d)
		Uniform, matt	Matt, seedy	Matt, pronounced sheeriness	Matt, uniform
75	Surface appearance				
	Clean-up properties	Very Good	Very Good	Very Good	Poor

Relative to paint sample (a), the film of paint sample (b) showed some seediness due to the presence at the surface of coarse particles of vesiculated granules. The paint sample (c), which contained an unduly high level of small diameter granules exhibited sheeriness. Although acceptable in other respects, the film of paint sample (d) picked up atmospheric dirt readily. Attempts to

remove the dirt by rubbing the film with a wet cloth resulted in marring of the film, in which the dirt appeared to have become firmly embedded. Furthermore, density measurements of the dry film showed it to be of higher density than that predicted, which would appear to be due to collapse of the vesiculated granules as the film dried.

*Example 21*

- A coating composition was prepared by dispensing rutile titanium dioxide (12.1 parts) in water (5 parts) in the presence of sodium hexametaphosphate (0.06 parts). The dispersion was then mixed with a latex of a 85/15 by weight copolymer of vinyl acetate and 2-ethyl hexyl acrylate (15 parts of latex of 50% solids content).
- To half of this coating composition was added a slurry in water of vesiculated granules made by the process described in example 3. (50 parts of slurry of 15% by weight granule content.).
- To the other half of the coating composition was added a slurry of granules (50 parts of a slurry of 30% by weight granule content) of the same composition and size but containing no vesicles.
- The two samples of coating composition were brushed out at a rate of 600 sq. ft. per gallon on Morest Charts. The opacity of the film of coating composition containing vesiculated granules was substantially greater than that of the film of the other sample of coating composition.

Similar results were obtained when a latex of poly (styrene-butadiene) and a latex of a styrene/acrylic acid/acrylate terpolymer were used in place of the acetate/acrylate latex.

Comparative coating compositions were also prepared by the above process using the same proportions of vesiculated granules according to the invention and prepared as described in examples 4, 5, 6, 7, 9, 10, 11, 12 and 14, and corresponding non-vesiculated granules. In each case a substantially higher degree of opacity was noted in films of compositions containing vesiculated granules as compared with non-vesiculated granules.

*Example 22*

- A coating composition was prepared by dispersing rutile titanium dioxide (12.1 parts) in water (5 parts) in the presence of sodium hexametaphosphate (0.06 part). The dispersion was then mixed with a latex of a commercial thermosetting acrylic copolymer (17 parts of latex of 46% by weight solids content).

To half of this coating composition was added a slurry in water of vesiculated granules made by the process described in example 7 (50 parts of slurry of 25% by weight granule content). Hydroxyethyl cellulose (10 parts of an aqueous solution of 2.25% solids content) was also added.

The coating composition was brushed out at a rate of 400 sq. ft. per gallon on a Morest Chart, and after allowing the film to dry at room temperature, it was baked at 100°C for two hours.

The opacity of the film of coating composition was significantly greater than that

of a control film in which the vesiculated granules had been replaced on an equal volume basis with granules of similar compositions and size, but containing no vesicles.

*Example 23*

A coating composition was prepared according to example 22 except that the acrylic latex was replaced with a water soluble alkyd (15 parts of alkyd solution of 50% solids content), and no hydroxyethyl cellulose was added.

A film brushed onto a Morest Chart had significantly better opacity on drying at room temperature than a control composition in which the granules were replaced an an equal volume basis with granules of similar composition and size, but containing no vesicles.

*Example 24*

A coating composition was prepared by dispersing rutile titanium dioxide (12.1 parts) in a dispersion in petrol of a 60/40 by weight copolymer of ethyl acrylate and methyl methacrylate (20 parts of the dispersion of 40% by weight solids content).

To half of this coating composition was added 12 parts of dry granules prepared by the process described in example 10, and 50 parts of petrol. The granules were dispersed in the composition using a high-speed stirrer, with the aid of sand. After removing the sand, the paint was sprayed onto a Morest Chart, and allowed to dry at room temperature. The film obtained was more opaque than a film of similar thickness prepared from a composition in which the vesiculated granules were replaced with the same volume of granules of similar composition and size, but containing no vesicles.

A similar result was obtained when the acrylic film-forming dispersion was replaced with a non-aqueous dispersion of a vinyl acetate copolymer.

*Example 25*

A coating composition was prepared by dispersing rutile titanium dioxide (10 parts) in a soya bean oil/glycerol phthalate alkyd (50% oil length) solution in mineral spirits (20 parts of a 40% by weight solution). Dry vesiculated unsaturated polyester/styrene copolymer granules (5 parts) prepared by the method given in example 17, and xylene (10 parts) were added to the dispersion, and the aggregates dispersed with sand using a high-speed stirrer.

After removal of the sand, the composition was brushed onto a Morest Chart at a rate of 600 square feet per gallon. The opacity of this film was significantly higher than a film of the same thickness in which the vesiculated granules had been replaced by an equal volume of granules of the same composition and size, but containing no

vesicles.

A similar result was obtained when the alkyd solution was replaced with a mixture of 15 parts of a solution in xylene of a 50/35/15 by weight copolymer of styrene, butyl acrylate and hydroxyethyl methacrylate, of solids content 40%, and 5 parts of a solution in xylene and butanol (1/1 by weight) of a butylated melamine formaldehyde resin of solids content 60% by weight. In this case the films were applied to the Morest Charts by spraying, and the coated charts were baked at 15°C for 30 minutes.

Similar results were obtained when the unsaturated polyester/styrene copolymer granules used in these two types of coating compositions were replaced by copolymer granules prepared by the method given in example 8.

#### Example 26

A coating composition was prepared by dispersing rutile titanium dioxide into a solution in a 1:1 by weight mixture of toluene and acetone of a 98/2 by weight methyl methacrylate/methacrylic acid copolymer solution (20 parts of a 40% by weight solution). Dry vesiculated unsaturated polyester/styrene copolymer granules (5 parts) prepared by the method given in example 7, acetone (10 parts), toluene (10 parts) and benzyl n-butyl phthalate (5 parts) were added to the dispersion and the aggregates dispersed by stirring at high-speed with sand.

After removal of the sand, the composition was sprayed onto a Morest Chart and after drying the film at room temperature for one hour the coated chart was baked at 150°C for 30 minutes. The opacity of this film was significantly higher than a film of the same thickness in which the vesiculated granules had been replaced by an equal volume of granules of the same composition and size, but containing no vesicles.

#### Example 27

Coating compositions were prepared by mixing the slurries of vesiculated granules (40 parts of the slurry) prepared by the method given in example 13 with a commercial acrylic aqueous latex (20 parts of the latex of solids content 46% by weight). The solids contents of the slurries and the granule porosities and average diameters are given in the table below:

Porosity of Granules	Average Diameter of Granules	Solids Content of Slurry
76	150	7.5
89	150	3.9
95	75	2.4

The coating compositions were spread onto wooden panels and allowed to dry. Textured white coatings were obtained. The coating containing the granules whose porosity was 96% of the total volume of the granules had unacceptable mechanical

properties, being very easily marred. These granules lie outside the limits of this invention.

#### Example 28

A coating composition was prepared by dispersing rutile titanium dioxide (25 parts) into a solution of a saturated polyester (hydroxyl content 10% by weight) in ethylene glycol monoethyl ether acetate (125 parts of the solution of solids content 30% by weight). Dry vesiculated granules (25 parts) prepared by the method given in example 7 were added to the dispersion, and the aggregates dispersed using sand with a high-speed stirrer.

After removal of the sand a hexamethylene diisocyanate adduct (isocyanate content 11.5% by weight) dissolved in a 1:1 by weight mixture of ethylene glycol acetate and xylene (75 parts of the solution of solids content 75% by weight) was added. The coating brushed onto a Morest Chart at a rate of 600 square feet per gallon, and allowed to dry for 72 hours at room temperature. The opacity of the film was significantly higher than a film of the same thickness in which the vesiculated granules had been replaced by an equal volume of granules of the same composition and size, but containing no vesicles.

A similar result was obtained when the saturated polyester solution was replaced with a solution of an epoxy resin (epoxide equivalence 500) in a 3:1 by weight mixture of ethylene glycol monoethyl ether and xylene (125 parts of a solution of solids content 40% by weight), and the hexamethylene diisocyanate adduct solution was replaced with a solution of a polyamide (amine value 215 mgm KOH per gram of polyamide) in a 1:1 by weight mixture of methyl isobutyl ketone, ethylene glycol monoethyl ether and xylene (50 parts of the solution of solids content 50%).

#### Example 29

This example illustrates the preparation of paper-containing vesiculated granules.

Dry wood pulp (10 parts) was mixed with water (190 parts) and the slurry beaten with a laboratory beater until uniform. A slurry of vesiculated granules (2 parts of the slurry of solid content 26% by weight) prepared by the method given in example 7 was added, and the beating process continued for a further 15 minutes. The slurry was further diluted with water (800 parts) and was fed into a paper-making machine.

The dry paper obtained had higher opacity than a similar composition in which the vesiculated granules had been omitted.

#### Example 30

This example illustrates the preparation of a sheet of polyethylene containing vesiculated granules.

Polyethylene granules (98 parts) were

5 blended with dry vesiculated granules (2 parts) prepared by the method given in example 7. To fully incorporate the vesiculated granules the mixture was extruded in the form of a tube, and fed into a granulator. The product was then extruded in the form of an opaque sheet of 1 mm thickness.

#### WHAT WE CLAIM IS:—

10 1. Vesiculated polymer granules wherein the granules have a mean diameter of at least 1 micron, the maximum diameter of the vesicles is less than 20 micron, the ratio of granule diameter to mean vesicle diameter is at least 5:1 and the volume of the vesicles is 5 - 95% of the total volume of the granules.

20 2. Granules as claimed in Claim 1 in which the volume of the vesicles is at least 20% of the volume of the granules.

3. Granules as claimed in Claim 1 or Claim 2 in which the diameter of the vesicles is less than 5 micron.

25 4. Granules as claimed in any one of Claims 1, 2 or 3 having a mean diameter of 1-50 micron.

30 5. Granules as claimed in any one of Claims 1 - 4 of which the volume average diameter of the granules is from 5 to 35 micron.

6. Granules as claimed in any one of Claims 1 - 5 in which the vesicles contain up to 60% by volume of particulate solid or liquid material.

35 7. Granules as claimed in Claim 6 in which the vesicles contain up to 45% by volume of solid or liquid material.

40 8. Granules as claimed in Claim 6 or Claim 7 in which the solid material is pigment.

9. Granules as claimed in any one of Claims 1 - 8 in which the polymer is cross-linked.

45 10. Granules as claimed in any one of Claims 1 - 9 which are spheroidal in shape.

11. Granules according to any one of Claims 1 - 10 wherein the polymer of the granule is pigmented at a concentration not exceeding the critical pigment volume concentration.

50 12. Granules as claimed in Claim 1 and substantially as herein described with reference to any one of Examples 1 - 15.

13. A coating composition comprising (a) a film-forming vehicle, (b) a pigment dispersed in the vehicle in a proportion of 0-85% of the total volume of (a) plus (b), and (c) insoluble vesiculated polymer granules as claimed in any one of Claims 1-12, said granules being dispersed in the composition in a proportion of from 5 to 95% of the total solids volume of the composition.

14. A coating composition as claimed in Claim 13 in which the proportion of vesiculated polymer granules is from 45 to 85% of the total solids volume of the composition.

15. A coating composition as claimed in Claim 13 or Claim 14 in which the pigment (b) is titanium dioxide in a proportion of from 10 to 35% of the volume of (a) plus (b).

16. A coating composition as claimed in any one of Claims 13-15 in which the film-forming vehicle (a) is a dispersion of a film-forming polymer in an aqueous liquid.

17. A coating composition as claimed in Claim 13 and substantially as described in any one of Examples 16-28.

18. Polymer containing dispersed therein vesiculated polymer granules as claimed in any one of Claims 1-12.

19. Paper containing dispersed therein vesiculated polymer granules as claimed in any one of Claims 1-12.

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